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Supporting Information for

Monodisperse Cylindrical Micelles and Block Comicelles of Controlled Length in Aqueous Media

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General Experimental Considerations

All air- or moisture-sensitive reactions were carried out in oven (200 °C) dried glassware under a positive nitrogen pressure using standard Schlenk techniques or in an MBraun MB150B-G glove box under nitrogen. Tetrahydrofuran (THF) for living anionic polymerizations and photochemical reactions was pre-dried with sodium and distilled off sodium/benzophenone prior to use. Anhydrous solvents were obtained using a modified Grubbs system of alumina columns manufactured by Anhydrous Engineering and degassed by bubbling nitrogen prior to use. Potassium hydride in paraffin was purchased from Sigma Aldrich and stored in a glove box under argon. Chlorodimethylvinylsilane was distilled prior to use. Allyl glycidyl ether was distilled off CaH_2 prior to use. All other commercially available compounds were used without further purification. The DNA strands were a commercially available native double-stranded DNA (purified from salmon testes, in its sodium salt form) containing ca. 2000 base pairs purchased from Sigma-Aldrich. Standard laboratory solvents were purchased from VWR or Fisher Scientific. Solvents for self-assembly were filtered (polytetrafluoroethylene membrane with 0.45 μm pore size) before use. Photoirradiation experiments were carried out with Pyrex-glass filtered emission from a 125 W medium-pressure mercury lamp (Photochemical Reactors Ltd.). An ethylene glycol/water bath in conjunction with a thermostat was used to maintain constant temperatures of 20 °C during the photoirradiation experiments. ^{1}H NMR spectra were recorded using Jeol Eclipse 400 MHz or Varian VNMR 400 MHz spectrometers. Thiol-functionalized triethylene glycol,[1] dimethylsila[1]ferrocenophane,[2] and PFS_{25}-*b*-$P2VP_{500}$[3] were synthesized as previously reported.

Polymer Characterization

Gel permeation chromatography was carried out on **1**, **3**, and **4** using a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with an automatic sampler, a pump, an injector, an inline degasser, and a column oven (30 °C). The elution columns consist of styrene/divinylbenzene gels with pore sizes between 500 Å and 100,000 Å. Detection was conducted by means of a VE 3580 refractometer, a four-capillary differential viscometer, and 90° and low angle (7°) laser light (λ_0= 670 nm) scattering detectors, VE 3210 & VE 270. THF (Fisher) was used as the eluent, with a flow rate of 1.0 mL/min. The calibration was conducted using a PolyCALTM polystyrene standard (PS115K) from

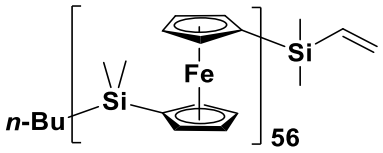
Viscotek. For PFS_{25}-*b*-$P2VP_{500}$ and its corresponding PFS aliquot, conventional calibration gel permeation chromatography (GPC-CC) measurements were carried out at 35 °C at a flow rate of 1.0 mL/min in nBu$_4$NBr/THF (0.1 % wt. nBu$_4$NBr) on a Viscotek GPCmax equipped with both a UV-Vis detector operating at 450 nm and differential refractometer. The column was calibrated with polystyrene standards. Samples were dissolved in the eluent (2 mg/mL) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of 0.45 μm pore size) before analysis. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurements of polyferrocenyldimethylsilane (PFDMS) were performed using a Bruker Ultraflextreme running in linear mode. Samples were prepared using a trans-2-(3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene) malononitrile matrix (20 mg mL^{-1} in THF) and the polymer sample (2 mg mL^{-1} in THF), mixed in a 10:1 (v/v) ratio. Approximately 1 μL of the mixed solution was deposited onto a MALDI sample plate and allowed to dry in air. The molecular weights of the diblock copolymers were then determined by combining the molecular weight M_n of the first block from MALDI-TOF measurements with the block ratio of the diblock copolymer obtained by integrating the ^{1}H NMR spectroscopic signal intensities of the respective blocks.

Transmission Electron Microscopy

Copper grids from Agar Scientific, mesh 400, were coated with a carbon film. Carbon coating was done using an Agar TEM Turbo Carbon Coater where carbon was sputtered onto mica sheets before deposition on the grids via flotation on water. The samples for electron microscopy were prepared by drop casting one drop (*ca.* 10 μL) of the micelle colloidal solution onto a carbon coated copper grid which was then placed on a piece of filter paper to remove excess solvent. Bright field TEM micrographs were obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. Images were analyzed using the ImageJ software package developed at the US National Institute of Health. For the statistical length analysis, a minimum of 200 cylinders were carefully traced by hand to determine the contour length. Histograms of the length distribution were constructed. From this data, values of the standard deviation of the length distribution "sigma" (σ) were determined. In addition, values of L_n and L_w of each sample were calculated as shown below (L = length of object, N = number).

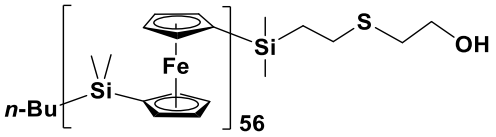
$$L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i} \qquad L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i L_i} \qquad \frac{L_w}{L_n} - 1 = (\frac{\sigma}{L_n})^2$$

Synthesis of vinyl-functionalized PFS_{56} (1)



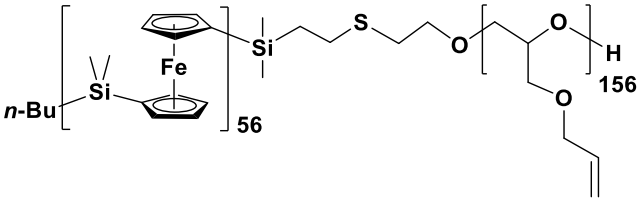
In a glove box under a nitrogen atmosphere 1.6 M *n*-butyllithium (24 µL, 40 µmol) was added in one portion to a vigorously stirred solution of dimethylsila[1]ferrocenophane (0.48 g, 2.0 mmol) in dry THF (3 mL). The reaction mixture was stirred for 1 h over which time the colour changed from red to orange. The solution was removed from the glove box, set up under a nitrogen atmosphere and the reaction was quenched with an excess of chlorodimethylvinylsilane. The crude product was precipitated in methanol (50 mL) and triethylamine (5 mL), precipitated twice more in methanol (2 × 50 mL) and dried *in vacuo* to afford the pure polymer (0.48 g, 97%) as an orange solid (87% end group functionalization by ^{1}H NMR).^{1}H NMR (400 MHz; CD_2Cl_2): δ_H 6.29 (dd, J = 20.3, 14.6 Hz, 1H, C*H*=CH_2), 5.99 (dd, J = 14.6, 3.8 Hz, 1H, CH=C*H*H-cis), 5.72 (dd, J = 20.3, 3.8 Hz, 1H, CH=C*H*H-trans), 4.23 (t, J = 1.7 Hz, 224H, Cp*H*), 4.03 (t, J = 1.7 Hz, 224H, Cp*H*), 0.48 (s, 336H, FcSi(C*H*$_3$)$_2$), 0.21 (s, Si(C*H*$_3$)$_2$, 6H) ppm.^{13}C NMR (101 MHz; CD_2Cl_2): δ_C 73.7 (Cp*C*), 72.2 (Cp*C*Si), 71.8 (Cp*C*), -0.8 (Si*C*H$_3$)$_2$ ppm. GPC: M_n = 13600 g/mol, PDI = 1.04. The degree of polymerization of this polymer was determined by a MALDI-TOF measurement (Figure S3).

Synthesis of hydroxyl-functionalized PFS_{56} (2)



To a solution of vinyl-terminated PFS_{56} (**1**) (0.20 g, 15 μmol) in dry THF (5 mL) was added 2,2-dimethoxy-2-phenylacetophenone (DMPA) (1.0 mg, 3.9 μmol) and 2-mercaptoethanol (20 μL, 0.15 mmol, approx. 10 equiv.) under a nitrogen atmosphere. The reaction mixture was sealed in a glass vial and irradiated 3 cm away from a mercury lamp for 1 h at 20 ℃. The solution was precipitated twice in methanol, once in hexane and dried *in vacuo* to afford the pure product as an orange solid (0.19 g, 96%) (70% end group functionalisation by ^{1}H NMR). ^{1}H NMR (400 MHz; CD_2Cl_2): δ_H 4.23 (t, J = 1.7 Hz, 224H, Cp*H*), 4.03 (t, J = 1.7 Hz, 224H, Cp*H*), 3.65 (app. q, J= 6.6 Hz, 2H, CH_2OH), 2.70 (app. t, J = 6.0 Hz 2H, SiCH$_2$CH_2), 2.59-2.53 (m, 2H SCH_2CH$_2$OH), 0.95-0.89 (m, 2H, SiCH_2), 0.48 (s, 336H, FcSi(CH_3)$_2$), 0.21 (s, Si(CH_3)$_2$, 6H) ppm. ^{13}C NMR (101 MHz; CD_2Cl_2): δ_C 73.7 (Cp*C*), 72.2 (Cp*C*Si), 71.8 (Cp*C*), -0.8 (Si*C*H$_3$)$_2$ ppm. GPC: M_n = 12200 g/mol, PDI = 1.04.

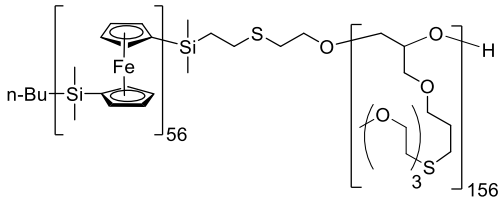
Synthesis of PFS_{56}-*b*-$PAGE_{156}$ BCP (3)



Hydroxyl-terminated PFS_{56} (**2**) (0.13 g, 7.1 × 10^{-3} mmol) was dissolved in dry THF (3 mL) in a greaseless Schlenk tube in a glove box under nitrogen. An excess of potassium hydride in paraffin (30 mg, 0.75 mmol) was added and the solution was stirred for 30 min. Allyl glycidyl ether (0.35 mL, 4.0 mmol) was added, the reaction mixture sealed under argon and heated at 45 °C for 16 h. The solution was filtered through a polytetrafluoroethylene membrane with 0.45 μm pore size and precipitated three times in hexane. The crude product was obtained in ca. 65-75% yield. Purification by preparative size exclusion chromatography (SEC), to remove any uncapped PFS homopolymer and unreacted **2**, afforded the pure

product **3** as an orange solid in ca. 20-35% yield. ^{1}H NMR (400 MHz; CD_2Cl_2): δ_H 5.90 (ddt, J = 16.1, 10.6, 5.4 Hz, 156H, C*H*=CH_2), 5.26 (dq, J = 16.1, 1.5, 156H, CH=C*H*H trans), 5.15 (dq, J = 10.6, 1.5, 156H, CH=C*H*H cis), 4.23 (t, J = 1.7 Hz, 224H, Cp*H*), 4.02 (t, J = 1.7 Hz, 224H, Cp*H*), 3.98 (d, J = 5.4 Hz, 312H, OC*H*$_2$CH=CH_2), 3.68-3.41 (m, 780H, C*H*$_2$C*H*C*H*$_2$), 0.48 (s, 336H, FcSi(C*H*$_3$)$_2$), ppm. ^{13}C NMR (101 MHz; CD_2Cl_2): δ_C 135.5 (*C*H=CH_2), 116.6 (CH=*C*H$_2$), 79.3-79.1 (*C*H$_2$ and *C*H), 73.5 (Cp*C*), 72.6 (Cp*C*Si), 72.1 (Cp*C*$_{ipso}$), 71.7 (Cp*C*), 70.7-70.1 (2*C*H$_2$), -0.9 (Si*C*H$_3$)$_2$ ppm. GPC: M_n = 25200 g/mol, PDI = 1.20. The degree of polymerization of the PAGE block was obtained by integrating the ^{1}H NMR spectroscopic signal intensities at 5.26 and 5.15 ppm (corresponding to the PAGE vinyl protons) and comparing them to those at 4.23 and 4.02 ppm (corresponding to Cp protons which were pre-determined by MALDI-TOF analysis of polymer **1**).

Synthesis of linear-brush PFS-*b*-(PEO-*g*-TEG) BCP (4)



To a solution of PFS_{56}-*b*-$PAGE_{156}$ (**3**) (20 mg, 6.4×10^{-4} mmol, 0.10 mmol vinyl) in dry THF (3 mL) was added thiol-functionalized triethylene glycol (90 mg, 0.50 mmol, ~5 eq. relative to vinyl groups) and DMPA (5 mg, 0.02 mmol). The orange solution was sealed under an argon atmosphere and irradiated 3 cm away from a mercury lamp for 2 h at 20 °C. The mixture was precipitated three times in hexane (~20 mL) and dried in vacuo to afford the pure block copolymer **4** (27 mg, 71%) as an orange gummy solid. ^{1}H NMR (400 MHz; CD_2Cl_2): δ_H 4.23 (t, J = 1.7 Hz, 224H, Cp*H*), 4.03 (t, J = 1.7 Hz, 224H, Cp*H*), 3.65-3.40 (m, 2652H, C*H*$_2$C*H*C*H*$_2$ and C*H*$_2$C*H*$_2$O), 3.34 (s, 468H, OC*H*$_3$), 2.69 (t, J = 8.0 Hz, 312H, OC*H*$_2$CH$_2$CH$_2$S), 2.61 (t, J = 8.0 Hz, 312H, OCH$_2$CH$_2$C*H*$_2$S), 1.83 (m, 312H, OCH$_2$C*H*$_2$CH$_2$S), 0.48 (s, 336H, FcSi(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz; CD_2Cl_2): δ_C 79.3 (*C*H), 73.6 (Cp*C*), 72.5 (Cp*C*Si), 71.8 (Cp*C*$_{ipso}$), 71.4 (Cp*C*), 71.0-70.4 (O*C*H$_2$ and S*C*H$_2$), 59.2 (O*C*H$_3$), 32.0 (OCH$_2$*C*H$_2$CH$_2$S), -0.8 (Si*C*H$_3$)$_2$ ppm. GPC: M_n = 70000 g/mol, PDI = 1.25.

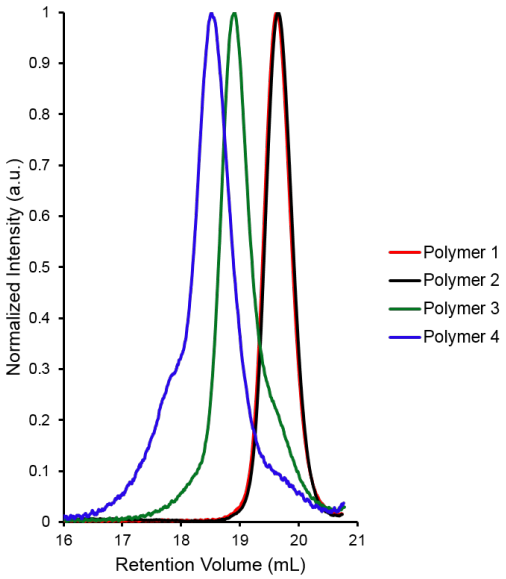


Figure S1. Overlaid refractive index GPC traces for PFS-*b*-(PEO-*g*-TEG) (**4**) (M_w/M_n = 1.25), PFS-*b*-PAGE (**3**) (M_w/M_n = 1.20), hydroxyl-terminated PFS homopolymer (**2**) (M_w/M_n = 1.04), and vinyl-terminated PFS homopolymer (**1**) (M_w/M_n = 1.04). The refractive index GPC traces for polymer **1** and **2** are coincident within experimental error. Note: the small high-molecular-weight shoulder observed in the RI trace for polymer **4** is suggestive of a small amount of vinyl coupling due to the steric bulkiness of the thiol used.[4]

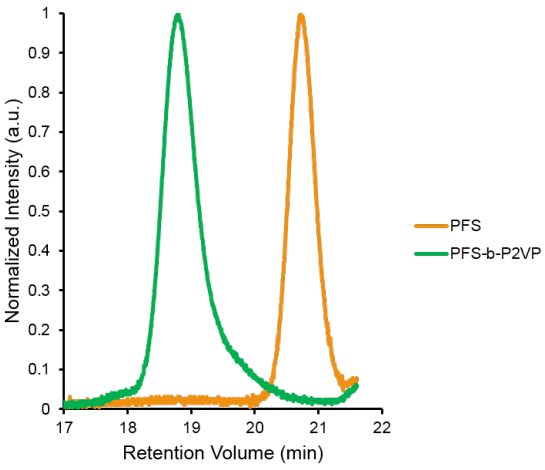


Figure S2. Overlaid refractive index GPC traces for PFS_{25}-*b*-$P2VP_{500}$ (M_w/M_n = 1.18) and its corresponding PFS aliquot (M_w/M_n = 1.14).

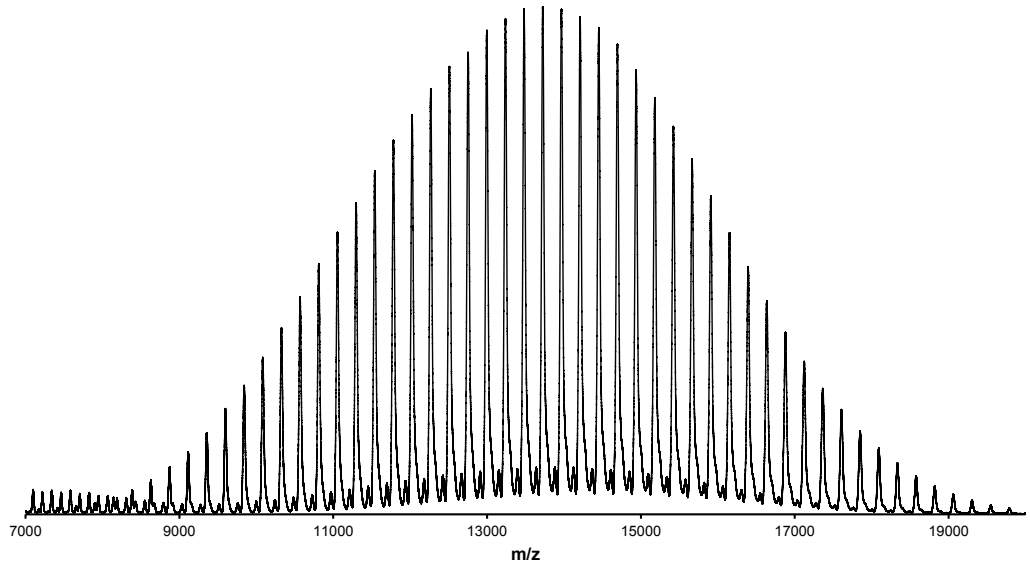


Figure S3. MALDI-TOF spectrum of polymer **1**. M_n = 13730.4 g/mol, M_w = 14026.9 g/mol.

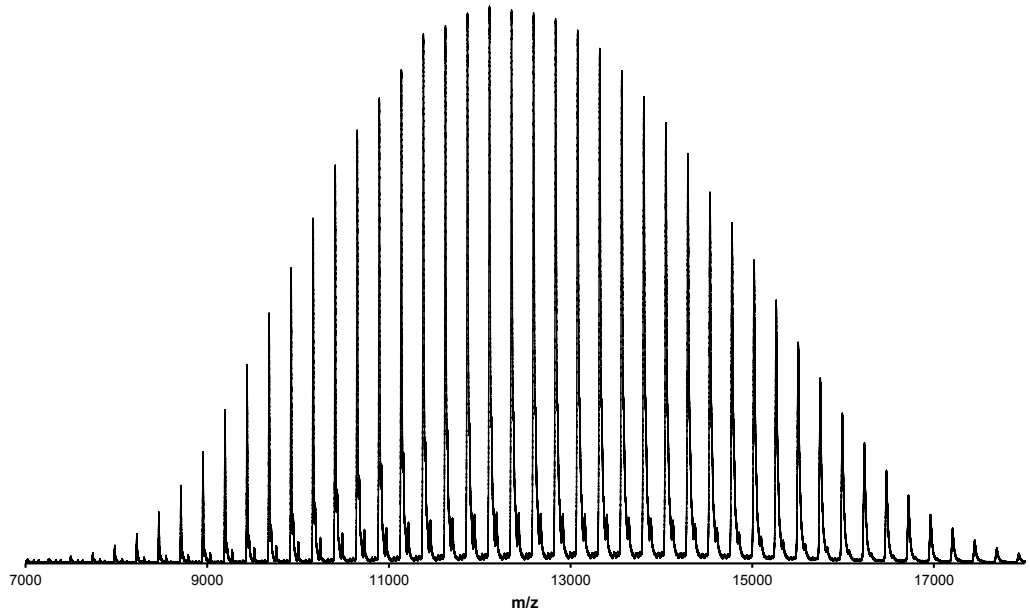


Figure S4. MALDI-TOF spectrum of polymer **2**. M_n = 13104.1 g/mol, M_w = 13359.5 g/mol. The apparent very slight decrease in M_n relative to that for polymer **1** (Figure S3) is within experimental error and may also arise from polymer purification procedures in which some material is sacrificed. The Refractive Index GPC traces for polymer **1** and **2** are identical within experimental error (See Figure S1).

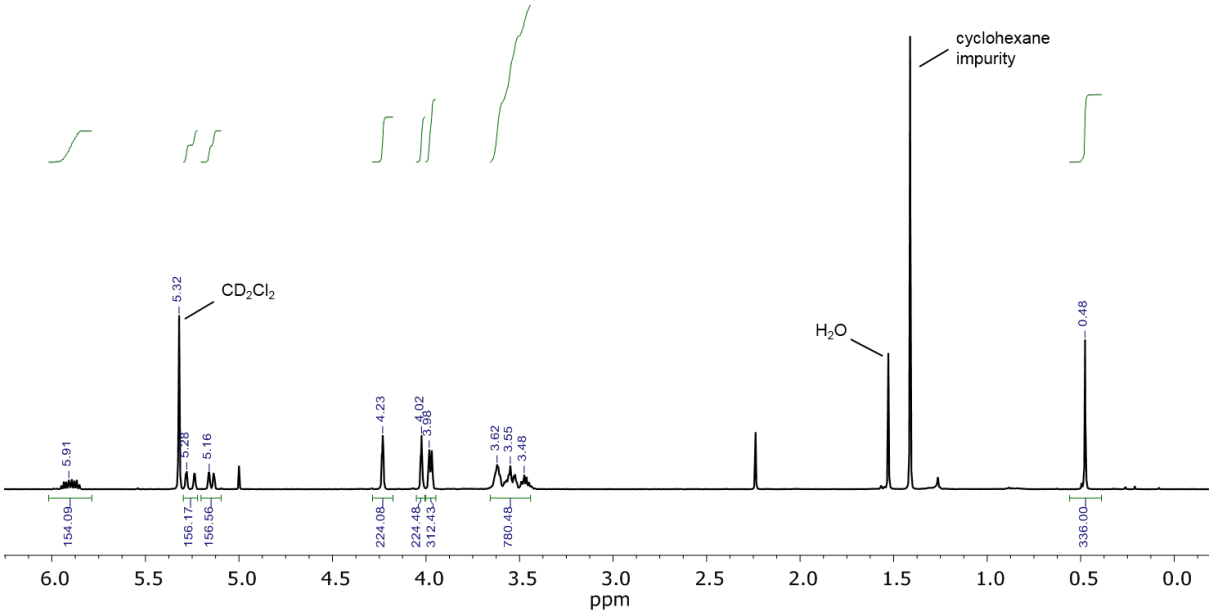


Figure S5. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) for polymer **3** (for peak assignments see the synthesis and characterization section above).

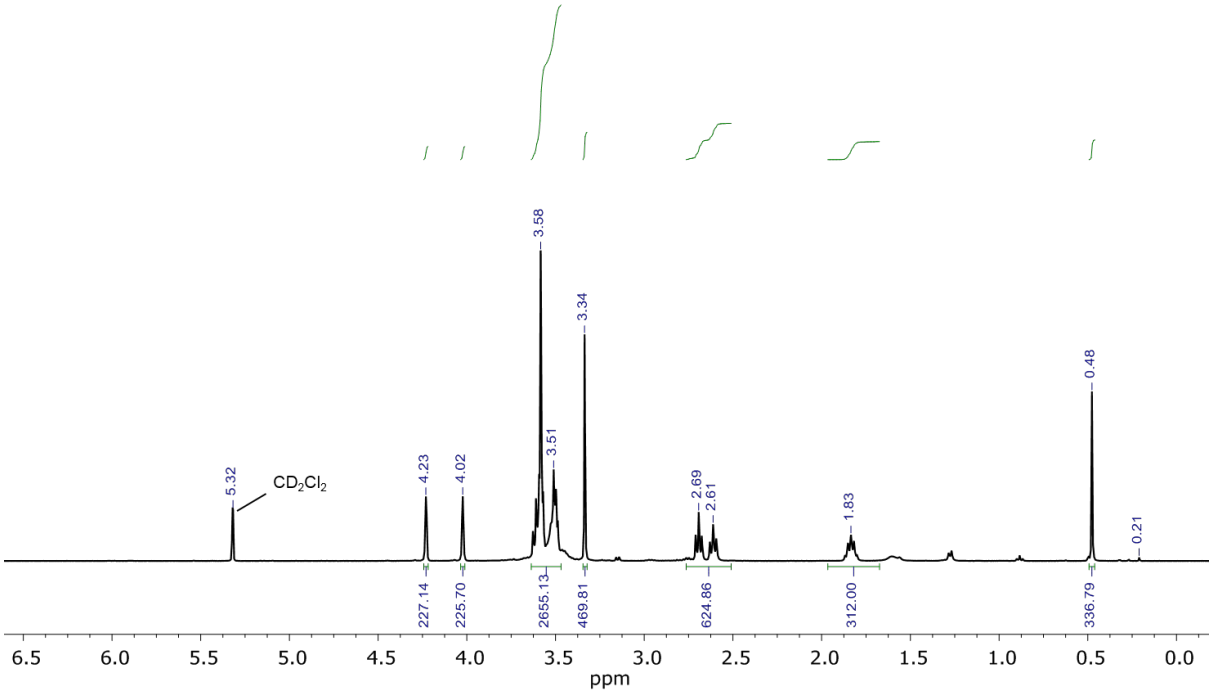


Figure S6. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) for polymer **4** (for peak assignments see the synthesis and characterization section above).

Preparation of micelles of 3 in ethyl acetate (EtOAc) and n-butanol (n-BuOH)

In two screw cap vials, polymer **3** was dissolved in EtOAc and n-BuOH at 75℃ and 110℃ at a concentration of 1 mg/mL, respectively, for 10 min. After this period of time, the samples were allowed to cool slowly to room temperature (22-25 ℃) and aged for two days. TEM analysis of the drop-cast samples on carbon-coated copper grids revealed the formation of polydisperse cylinders in both solvents (Figure S7).

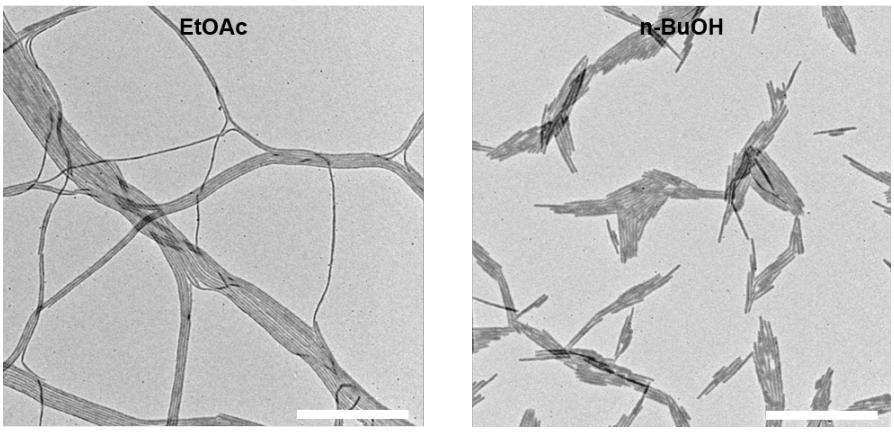


Figure S7. TEM micrographs of polydisperse cylinders of **3** formed in EtOAc (left) and n-BuOH (right). Scale bars 1000 nm.

Preparation of micelles of 4 directly in water

Method A – Addition of THF solution of **4** into water: To 0.95 mL of deionized (DI) water was quickly injected 0.5 mg of BCP **4** as solution in THF (10 mg/mL, 50 μL). The vial was capped and left to stand for over two months. Aliquots of the sample were drop-cast on carbon-coated copper grids at different time points.

Morphological transitions of the sample prepared via Method A are shown in Figure S8.

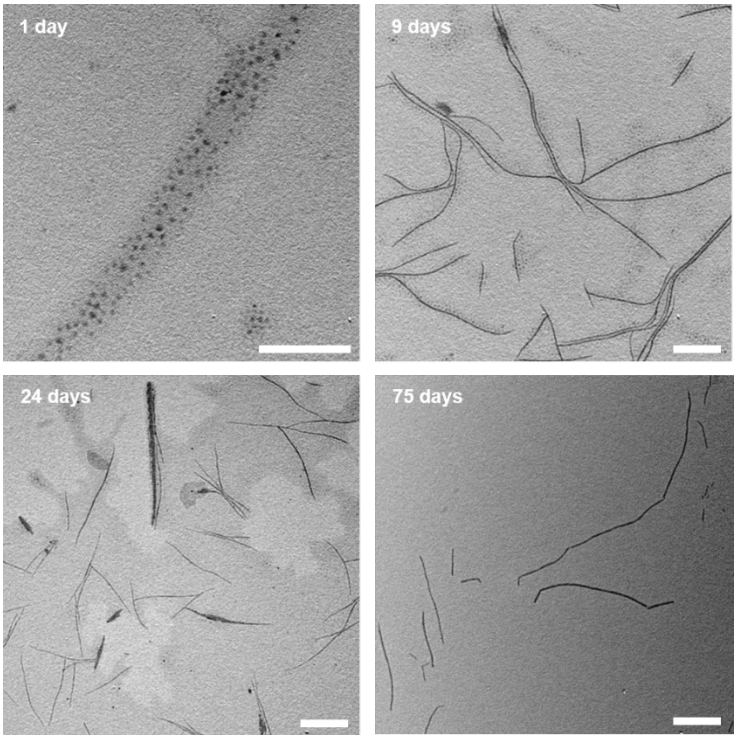


Figure S8. TEM micrographs of morphological transitions when a THF solution of **4** (10 mg/mL, 50 µL) is rapidly injected into DI water (0.95 mL). Cylindrical micelles are exclusively observed after about 75 days. Scale bars 500 nm.

Method B - Addition of water to THF solution of **4**: To THF solution of **4** (10 mg/mL, 50 µL) was added DI water (0.95 mL, 15 µL/min) to obtain a final concentration of 0.5 mg/mL. The vial was capped and left to stand for over two months. Aliquots of the sample were drop-cast on carbon-coated copper grids at different time points. Two representative TEM micrographs of this sample are shown in Figure S9.

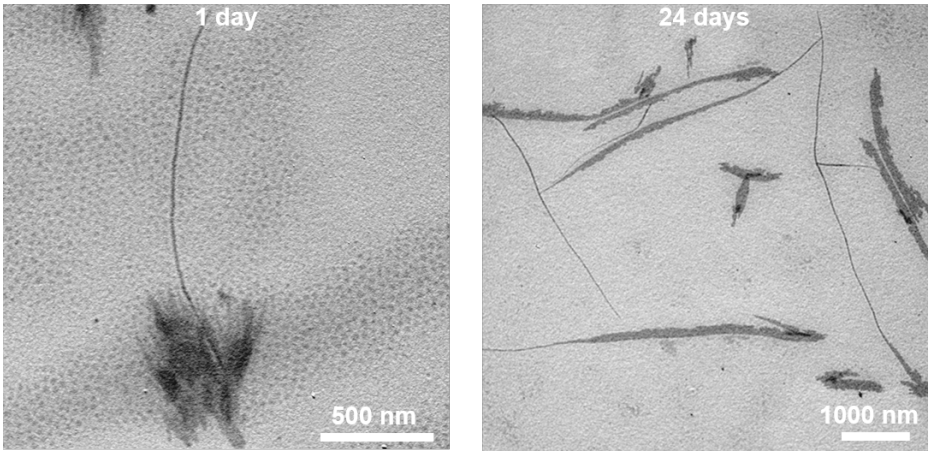


Figure S9. TEM micrographs of self-assembled materials obtained when to THF solution of **4** (10 mg/mL, 50 µL) was added DI water (0.95 mL, 15 µL/min).

Method C - Self-assembly of **4** in water/THF at elevated temperature: A suspension of BCP **4** (0.5 mg) in water (0.95 mL) / THF (50 μL) was heated to 95℃ for 2 h followed by slowly cooling of the sample to room temperature and its subsequent aging for two days. Aliquots of the sample were drop-cast on carbon-coated copper grids at different time points. Two representative TEM micrographs of this sample are shown in Figure S10.

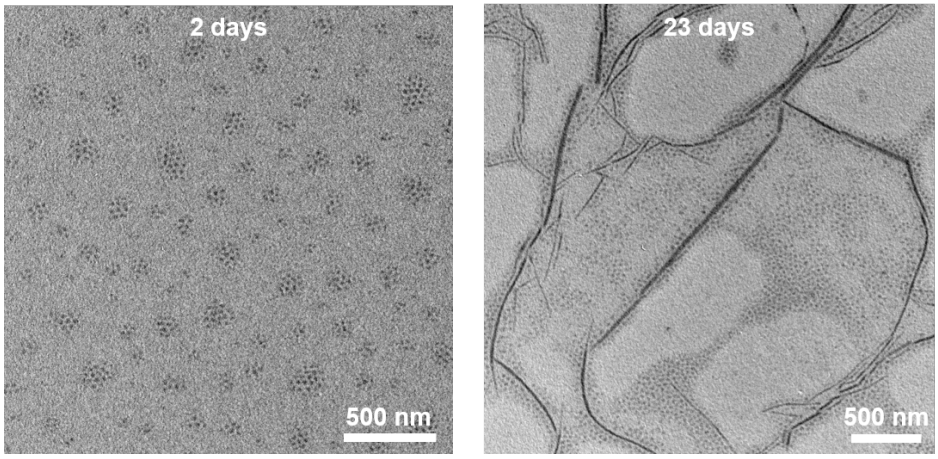


Figure S10. TEM micrographs of self-assembled materials obtained when a suspension of BCP **4** (0.5 mg) in water (0.95 mL) / THF (50 μL) was heated to 95℃ for 2 h followed by slowly cooling of the sample to room temperature and its subsequent aging for two days.

Method D – Slow evaporation of THF from BCP **4** solution in THF/H_2O: Polymer **4** (0.5 mg) was dissolved in a mixture of THF (2 mL) and DI water (1 mL) in a 7 mL screw cap vial at room temperature (22-25℃). The vial was covered with a Kimwipe tissue and left to stand for 4 days (note that longer times result in the evaporation of water as well). During this time, THF was slowly evaporated. TEM analysis of an aliquot of the sample showed the predominant formation of spherical micelles and the presence of small amount of cylinders. A few representative TEM micrographs of this sample are shown in Figure S11.

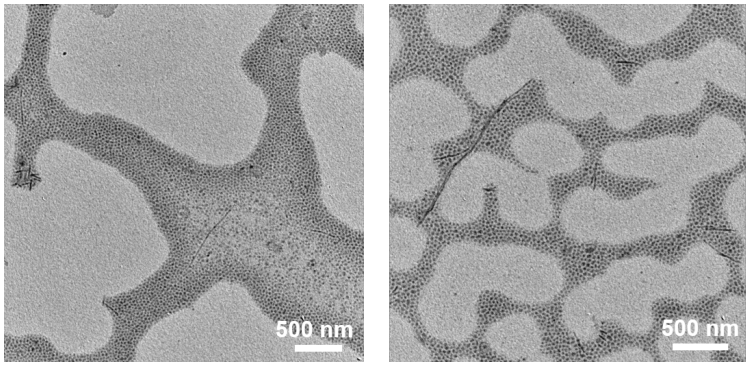


Figure S11. TEM micrographs of self-assembled materials obtained by slow evaporation of THF from the BCP **4** (0.5 mg) solution in a mixture of H_2O and THF (H_2O:THF, 1:2, 3 mL) over a period of four days.

Self-assembly of BCP 4 in organic solvents at elevated temperatures

In six separate vials, polymer **4** was dissolved in methanol (MeOH), ethanol (EtOH), *iso*-propanol (i-PrOH), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 1,4-dioxane at 60℃, 75℃, 80℃, 110℃, 90℃ respectively at the concentration of 0.5 mg/mL for 1 h. After this period of time, the samples were allowed to cool slowly to room temperature (22-25℃) and aged for two days. TEM analysis of the drop-cast samples on carbon-coated copper grids showed either the formation of spherical micelles or the presence of unimer film (Figure S12).

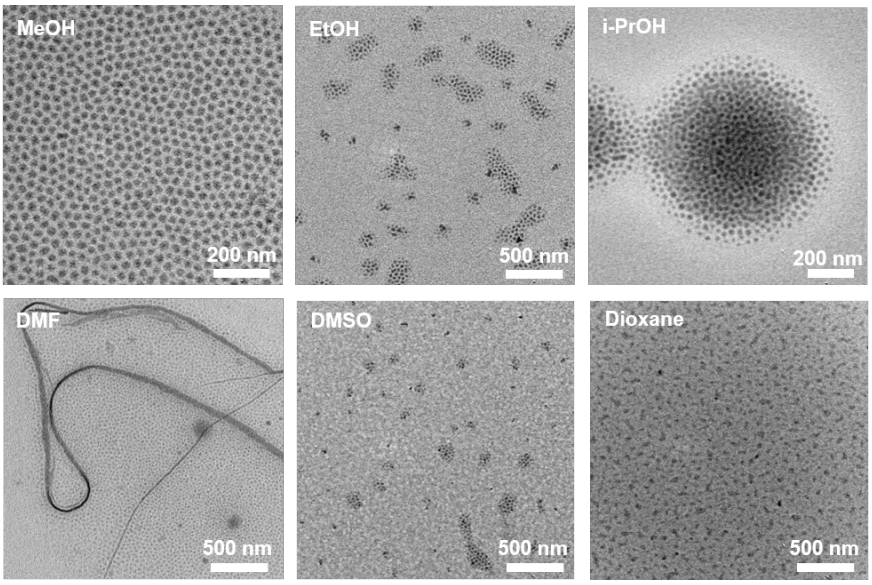
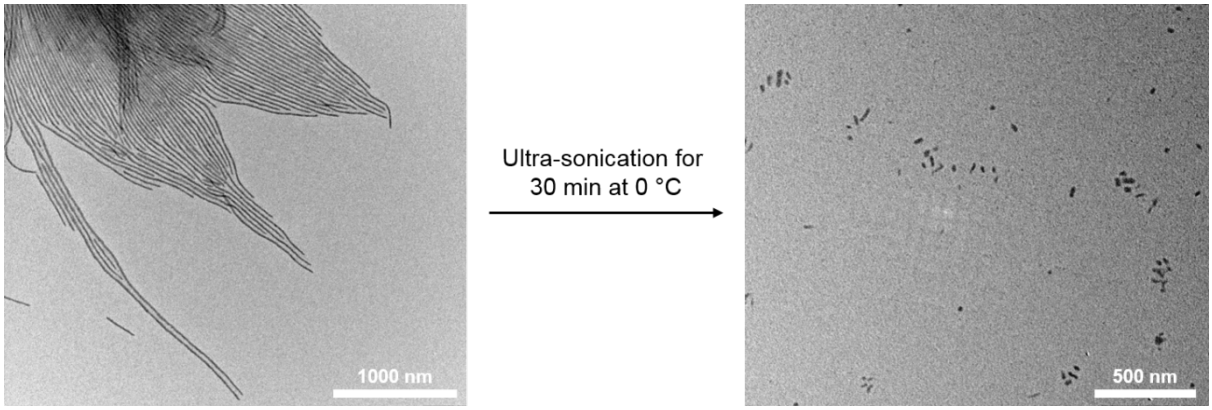


Figure S12. TEM micrographs of self-assembled materials obtained from polymer **4** in various solvents at elevated temperatures: MeOH (60℃), EtOH (75℃), i-PrOH (80℃), DMF (110℃), DMSO (110℃), and dioxane (90℃).

Preparation of long cylinders of 4 in DMF and their subsequent sonication to form seed micelles

Polymer **4** (0.5 mg) was dissolved in a mixture of THF (2 mL) and DMF (1 mL) in a 7 mL screw cap vial at room temperature (22-25℃). The vial was covered with a Kimwipe tissue and left to stand for one week. During this time THF was slowly evaporated. TEM analysis of an aliquot of the sample showed the formation of long, polydisperse cylinders. To form seed micelles, the long cylinders were subjected to sonication at 0 °C in an ice bath for 30 min using a probe ultrasonic processor (Hielscher UP50H operating at 30 kHz and 50 W equipped with a Hielscher MS1 titanium sonotrode).



Small- and wide angle X-ray scattering (SAXS and WAXS)

The X-ray diffraction data was taken with a Ganesha small angle X-ray scattering apparatus (SAXSLAB, Denmark). The instrument uses copper K alpha radiation (1.5 Å) and the scattering pattern is detected by Pilatus 300K X-Ray Detector (Dectris, Switzerland). The detector was placed at approximately 950 mm and 100 mm from the sample for the SAXS and WAXS measurements respectively. Samples were prepared at 5 mg/mL in DMF and sealed into 1.5 mm diameter quartz capillary tubes (Capillary Tube Supplies, Cornwall, UK). The instrument was evacuated during measurements to reduce air scattering.

The strong and broad negative peaks in the WAXS intensity of both samples are a result of the solvent subtraction; often solutes at sufficiently high concentration will affect the interparticle interactions of the solvent. This effect is particularly strong in highly polar and strongly hydrogen-bonded solvents such as DMF. The resulting slight mismatch in the

position and amplitude of the intermolecular solvent correlation peaks therefore gives rise to negative values on subtraction.

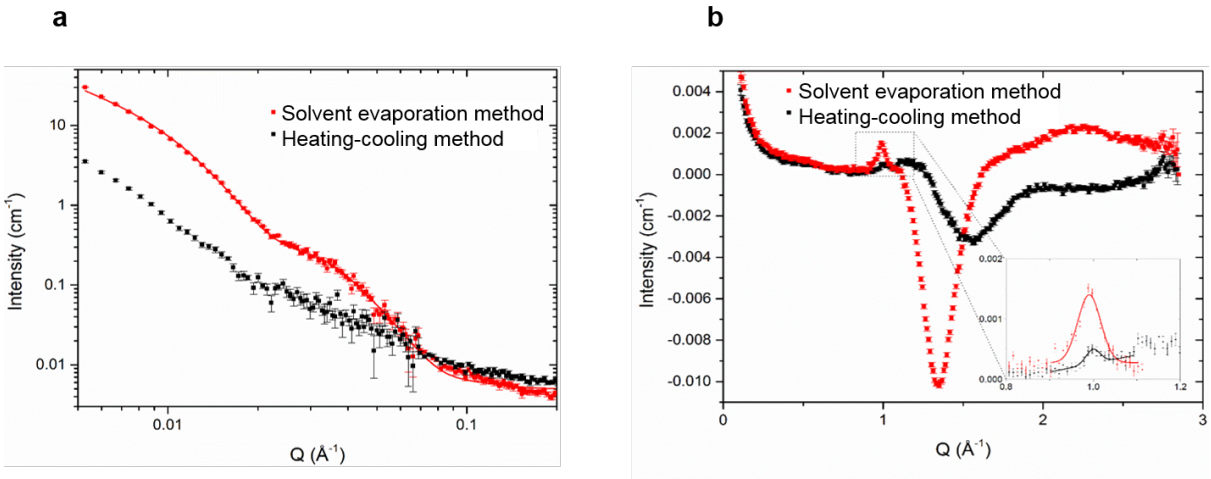
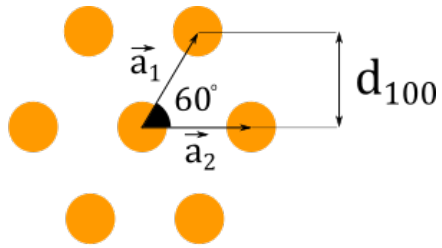


Figure S13. Azimuthally averaged intensity from (a) small- and (b) wide angle X-ray scattering from assemblies formed by polymer **4** in DMF (5 mg/mL).

The interchain packing distance of 7.3 Å was calculated as follows:

Hexagonal packing of polyferrocenylsilane chains viewed in direction parallel to the length of the chains (i.e. perpendicular to the long axis of the micelles) is shown in the diagram below.[5] The value of d_{100} was taken as 6.3 nm from the WAXS data and the value for the interchain packing (equivalent to the magnitude of the a_1 and a_2 vectors) is given by a simple geometric relation.



$$|\vec{a}_1| = |\vec{a}_2| = \frac{d_{100}}{\sin(60)}$$

Seeded growth of polymer 4 in DMF and its subsequent dialysis against water

To seven separate 1.5 mL screw cap vials was added 20 µL of a 0.5 mg/mL solution of seed micelles (10 µg, L_n = 38 nm, L_w = 45 nm, L_w/L_n = 1.20, σ/L_n = 0.45) and DMF (0.2 mL). To these solutions was added 10 µg, 25 µg, 50 µg, 100 µg, 150 µg, 200 µg, and 300 µg of

polymer **4** dissolved in THF (10 mg/mL). After shaking the vial for 5 s, the solutions were aged for 48 h at 22-25℃. Multiple TEM images were obtained and the contour lengths were measured from 200 – 250 micelles.

To transfer the cylinders from DMF into water, each sample was separately placed in a 3500 g/mol molecular weight cut-off (MWCO) membrane and dialyzed against DI water (200 mL) for 24 h with two changes of the dialysate. Size measurement data for cylinders in water and DMF are summarized in Table 1 in the main text.

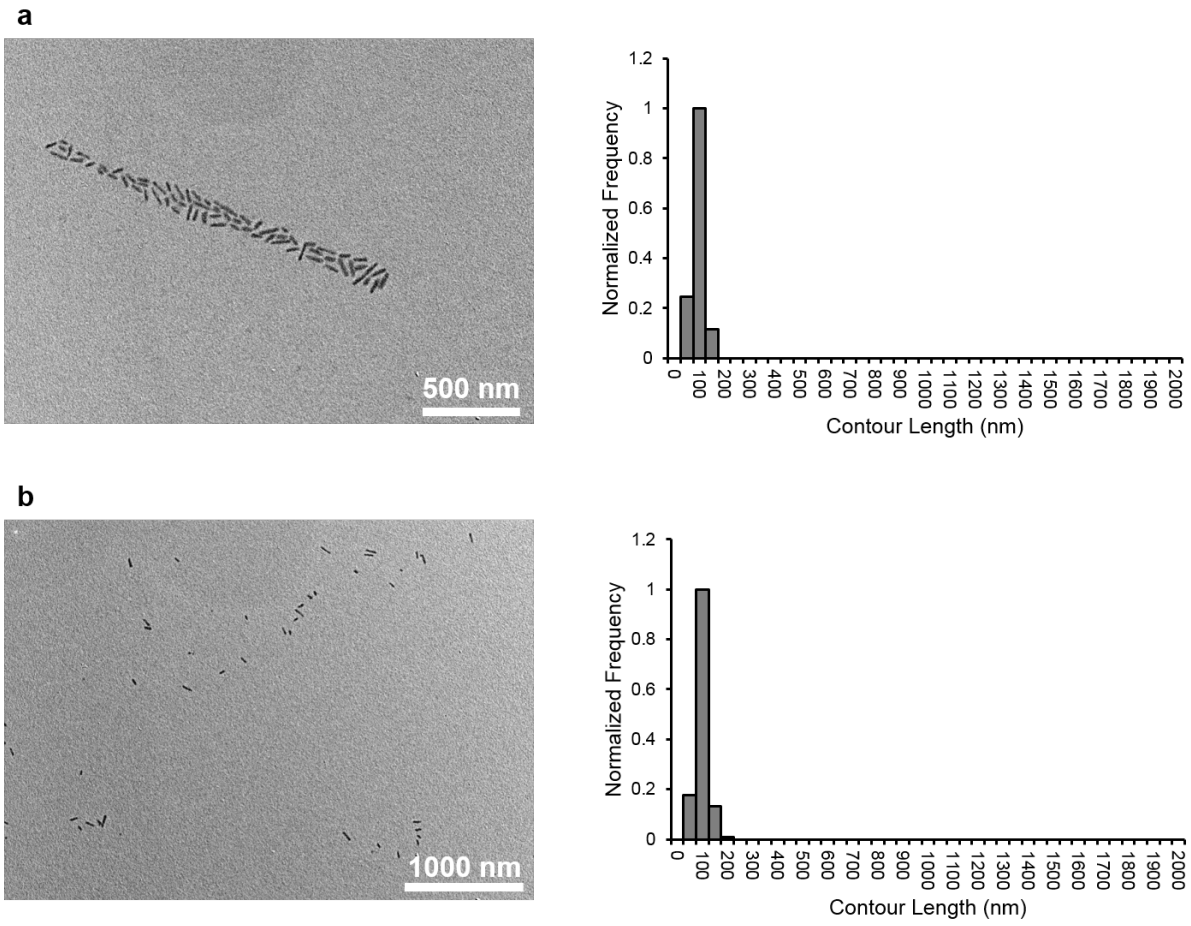


Figure S14. TEM micrograph of cylinders formed by the addition of 10 μg of polymer **4** to 10 μg of seeds in DMF (left) and length histogram of the resulting cylindrical micelles (right): (a) before dialysis against water (L_n = 71 nm, L_w = 78 nm, L_w/L_n = 1.10, σ/L_n = 0.31), (b) after dialysis against water (L_n = 69 nm, L_w = 75 nm, L_w/L_n = 1.10, σ/L_n = 0.31).

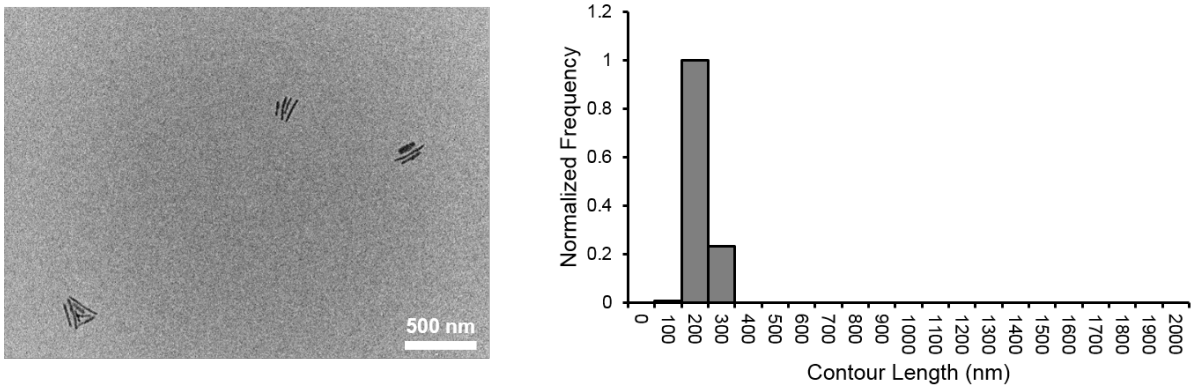


Figure S15. TEM micrograph of cylinders formed by the addition of 25 μg of polymer **4** to 10 μg of seeds in DMF (left) and length histogram of the resulting cylindrical micelles (right).

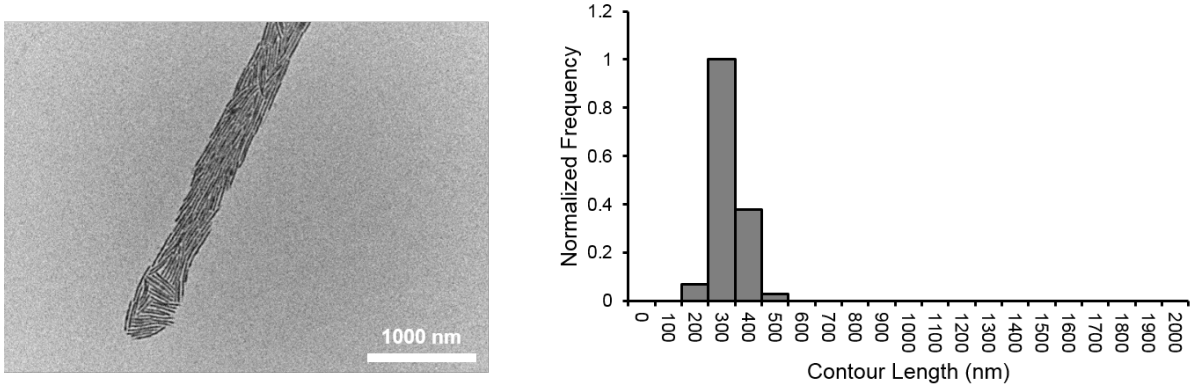


Figure S16. TEM micrograph of cylinders formed by the addition of 50 μg of polymer **4** to 10 μg of seeds in DMF (left) and length histogram of the resulting cylindrical micelles (right).

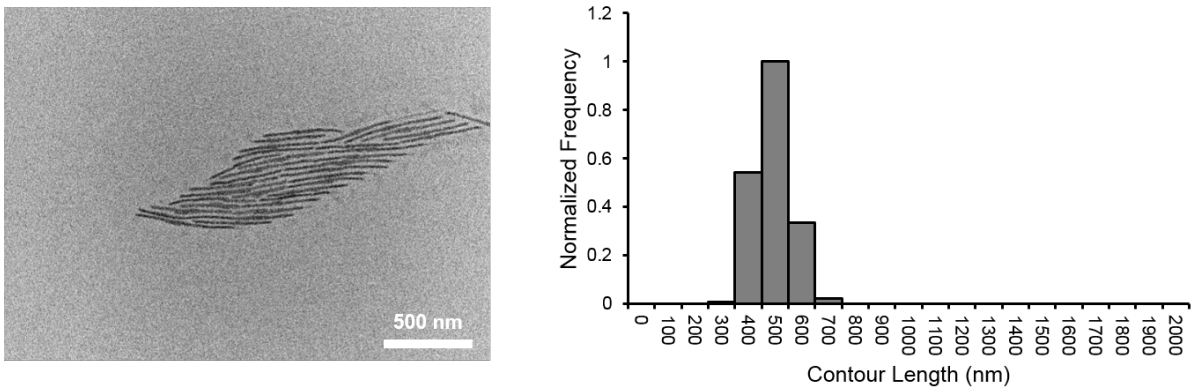


Figure S17. TEM micrograph of cylinders formed by the addition of 100 μg of polymer **4** to 10 μg of seeds in DMF (left) and length histogram of the resulting cylindrical micelles (right).

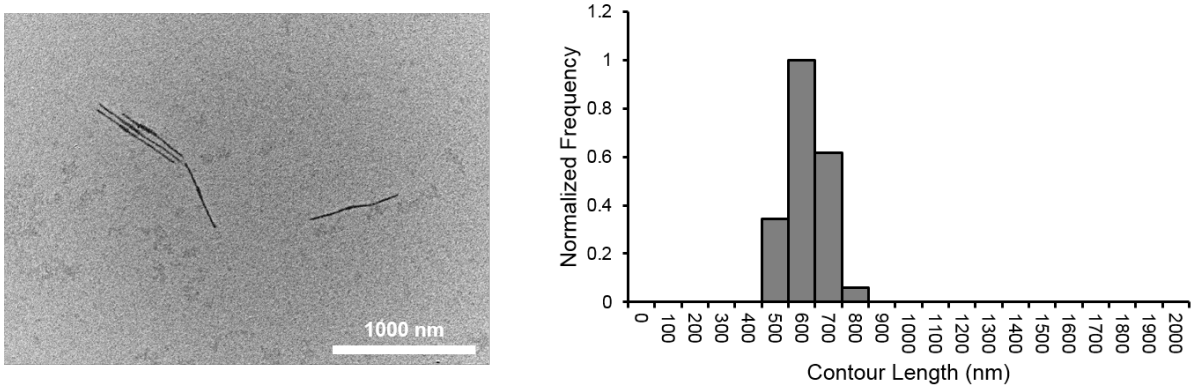


Figure S18. TEM micrograph of cylinders formed by the addition of 150 μg of polymer **4** to 10 μg of seeds in DMF (left) and length histogram of the resulting cylindrical micelles (right).

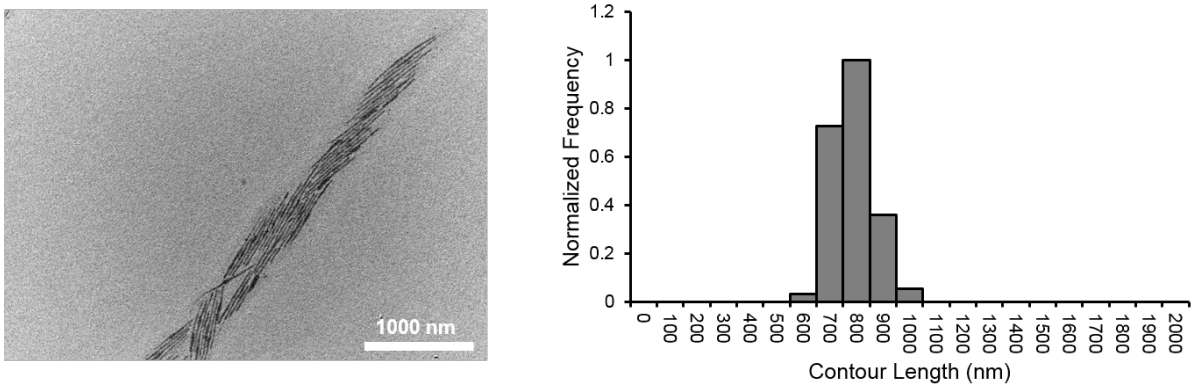


Figure S19. TEM micrograph of cylinders formed by the addition of 200 μg of polymer **4** to 10 μg of seeds in DMF (left) and length histogram of the resulting cylindrical micelles (right).

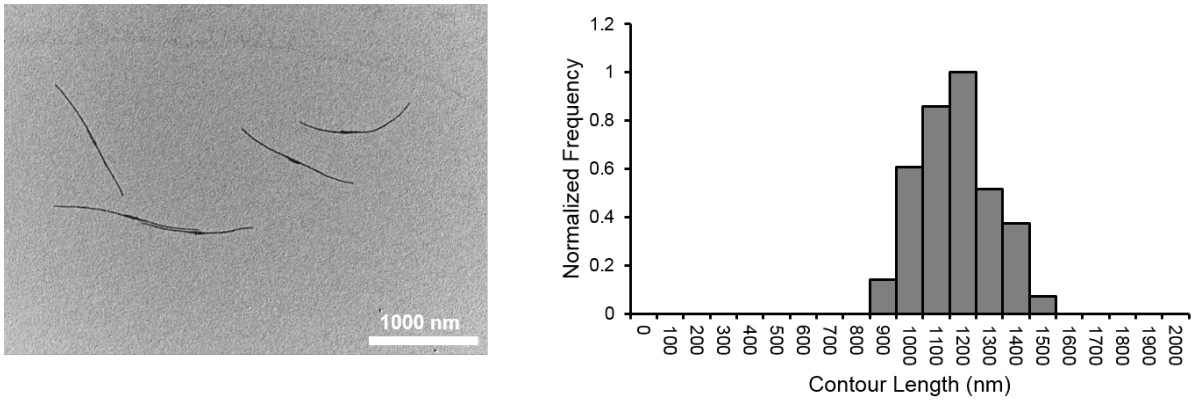


Figure S20. TEM micrograph of cylinders formed by the addition of 300 μg of polymer **4** to 10 μg of seeds in DMF (left) and length histogram of the resulting cylindrical micelles (right).

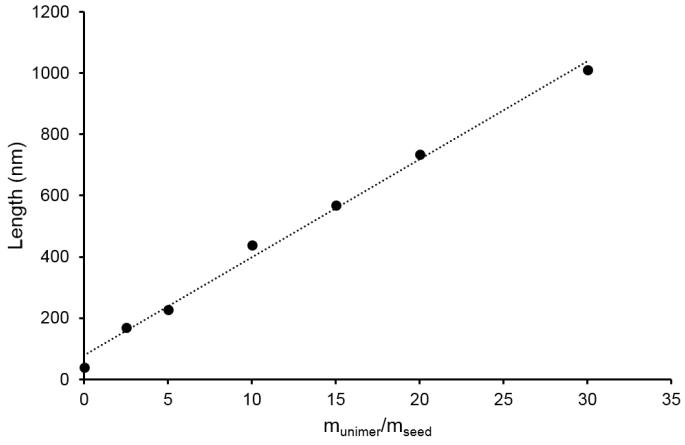


Figure S21. Graph demonstrating the linear dependence of cylinder length on m_{unimer}/m_{seed} in DMF.

Attempted seeded growth in aqueous media

To a 1.5 mL screw cap vial was added 20 μL of a cylindrical micelle solution in DI water (0.27 mg/mL, L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) and DI water (0.2 mL). To this solution was added 27 μg of polymer **4** dissolved in THF (10 mg/mL). After shaking the vial for 5 s, the solutions were aged for 4 days at 22-25℃. TEM analysis revealed the presence of random populations of cylinders that did not undergo seeded growth, those grown from only one terminus, ones unevenly grown from both termini, and cylinders formed via spontaneous nucleation (Figure S22).

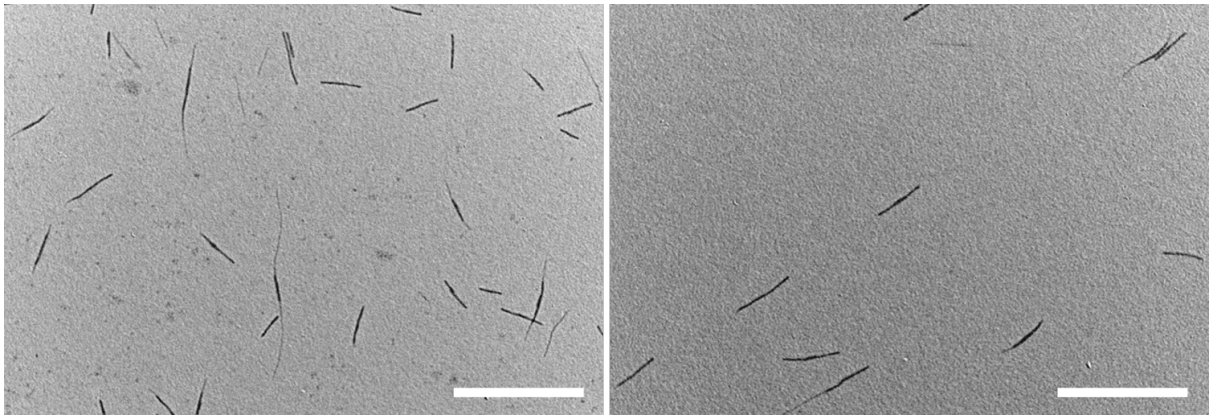


Figure S22. TEM micrograph of cylinders formed by the addition of 27 μg of polymer **4** as a solution in THF (10 mg/mL) to 5.4 μg of cylinders in DI water (L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24). Cylindrical micelles with lower contrast are those formed after the unimer addition to seed micelles. Scale bars 1000 nm.

Aggregation number of block copolymers in PFS-*b*-(PEO-*g*-TEG) homomicelles

Using the data obtained by SAXS and WAXS analysis, we were able to estimate the aggregation number of block copolymer chains for each PFS-*b*-(PEO-*g*-TEG) cylindrical homomicelle as follows:

Previous experiments have shown that PFS chains fold and pack in a direction perpendicular to the long axis of the micelles.[6] Therefore, by taking the ratio of the average diameter of the core (7.3 nm as obtained by SAXS measurements) to the average d-spacing (0.63 nm as obtained from the WAXS measurements) one finds a value of 11.6 folded polymer segments spanning the diameter of the crystalline core. The average length of each of these polymer segments is 5.7 nm, found by taking the ratio of cross-sectional area to diameter. This gives a total segment length of 66.4 nm per unit cell slice of the cross-section.

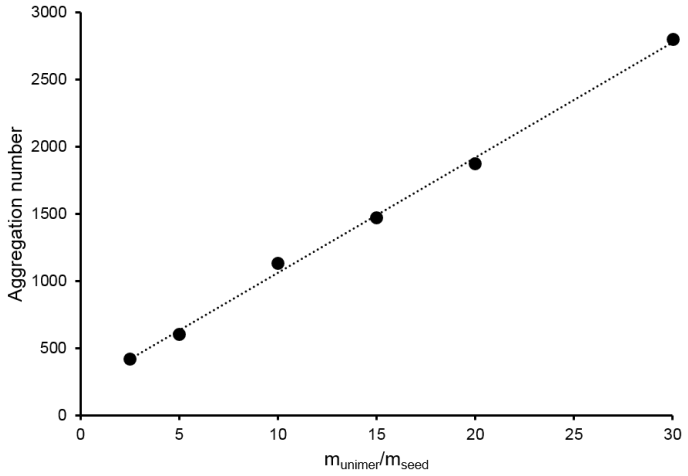
The contour length of the core chains is based on the number-average degree of polymerization of the PFS block in PFS-*b*-(PEO-*g*-TEG) (56 as determined by GPC) and the average intramolecular Fe-Fe distance in PFS (0.64 nm).[6] This gives an average chain length of 35.8 nm. Finally, by taking the ratio of the total segment length to average chain length, one arrives at a value of 1.85 PFS chains per unit cell slice of the cross-section. In order to make this comparable to other systems, one can divide by the interchain spacing for a hexagonal unit cell (7.3 nm, as obtained by fitting the azimuthally averaged SAXS data to the

model for a long cylinder of circular cross-section and constant electron density with a corona of decaying electron density) to give the number of chains per unit length, in this case 2.5 chains/nm which is in a good agreement with previous findings.[7]

Based on the number of chains per unit length and the L_n values for each PFS-*b*-(PEO-*g*-TEG) cylindrical micelle, their corresponding aggregation numbers ($N_{aggr.}$) are summarized in the table below:

L_n (nm)	167	240	449	583	741	1107
$N_{aggr.}$	422	607	1136	1475	1875	2801

As can be seen in the plot below, there is a linear relationship between m_{unimer}/m_{seed} and aggregation number.



Please note that same calculations were not performed for block comicelles as the PFS chain length and presumably the core radii of the two blocks would be different.

Preparation of B-A-B amphiphilic triblock comicelles

To three separate 1.5 mL screw cap vials was added 80 µL of a 0.267 mg/mL solution of PFS-*b*-(PEO-*g*-TEG) cylindrical micelles (20 µg, L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) in DMF and i-PrOH (0.4 mL). To these solutions was added 10, 20, and 40 µg of PFS_{25}-*b*-$P2VP_{500}$ dissolved in THF (10 mg/mL). After shaking the vial for 5 s, the solutions

were aged for 24 h at 22-25℃. Multiple TEM images were obtained and the contour lengths were measured from 200 – 250 fibres.

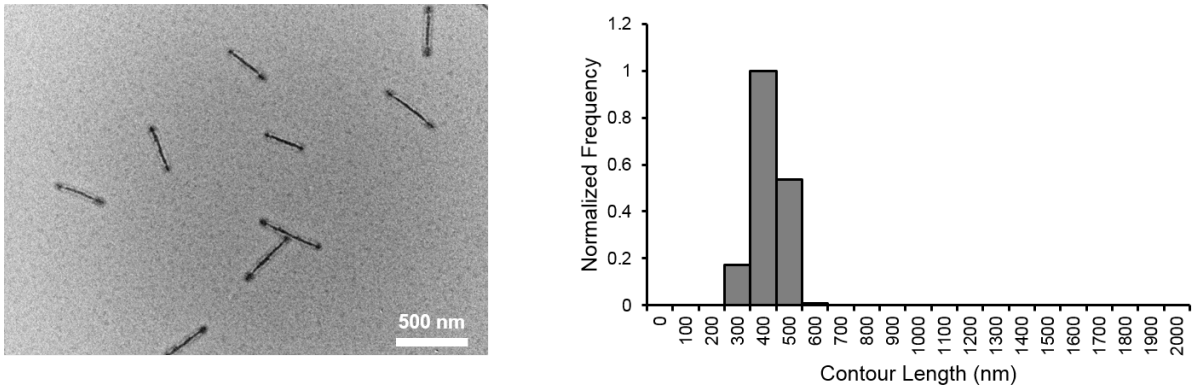


Figure S23. TEM micrograph of triblock comicelles (L_n = 371 nm, L_w = 381 nm, L_w/L_n = 1.02, σ/L_n = 0.16) formed by the addition of 10 μg of PFS_{25}-*b*-$P2VP_{500}$ to 20 μg of PFS-*b*-(PEO-*g*-TEG) cylinders in i-PrOH (L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) (left) and length histogram of the resulting cylindrical micelles (right).

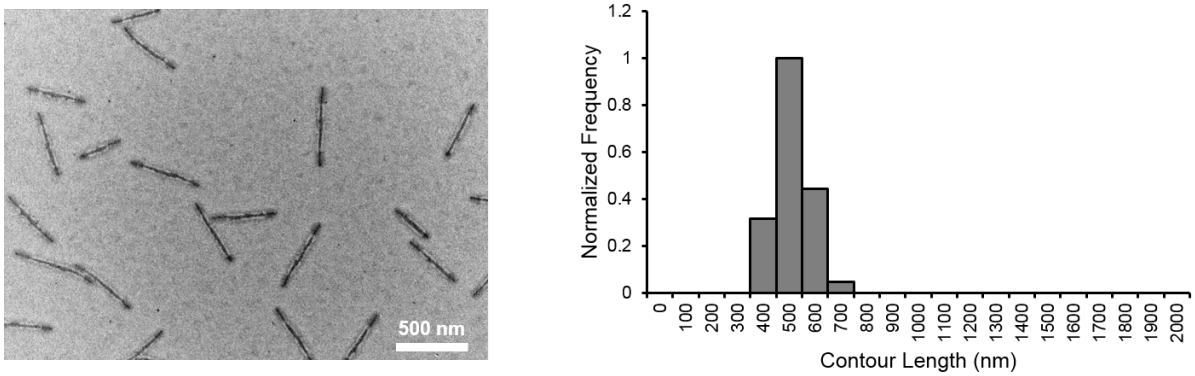


Figure S24. TEM micrograph of triblock comicelles (L_n = 459 nm, L_w = 469 nm, L_w/L_n = 1.02, σ/L_n = 0.14) formed by the addition of 20 μg of PFS_{25}-*b*-$P2VP_{500}$ to 20 μg of PFS-*b*-(PEO-*g*-TEG) cylinders in i-PrOH (L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) (left) and length histogram of the resulting cylindrical micelles (right).

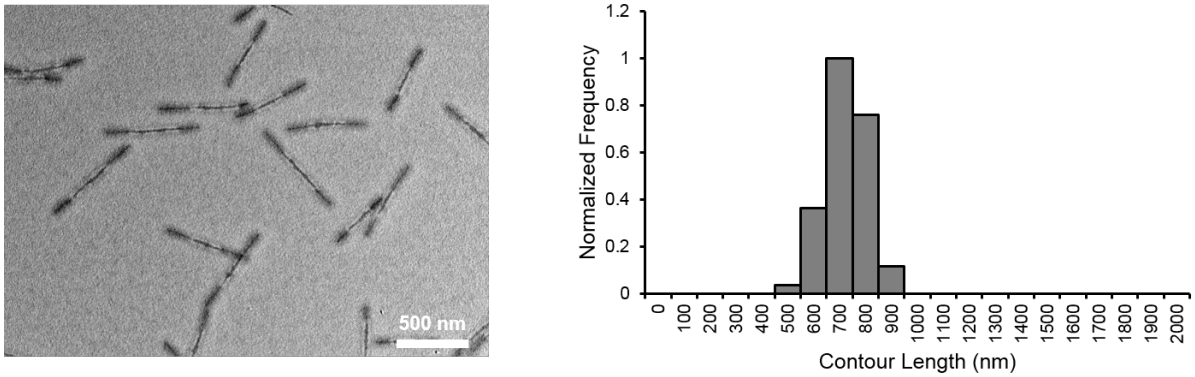


Figure S25. TEM micrograph of triblock comicelles (L_n = 675 nm, L_w = 684 nm, L_w/L_n = 1.01, σ/L_n = 0.12) formed by the addition of 40 μg of PFS_{25}-*b*-$P2VP_{500}$ to 20 μg of PFS-*b*-(PEO-*g*-TEG) cylinders in i-PrOH (L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) (left) and length histogram of the resulting cylindrical micelles (right).

Hierarchical self-assembly and disassembly of B-A-B amphiphilic triblock comicelles in aqueous media

To 0.2 mL of the triblock comicelles in i-PrOH was added DI water (1 mL) and the resulting samples were aged for 24 h. Subsequently, each sample was transferred to a 3500 g/mol MWCO dialysis membrane and dialyzed against DI water (200 mL) for 24 h with two changes of the dialysate. An aliquot of each sample was drop-cast on carbon-coated TEM grid for imaging.

Quaternization-induced disassembly was achieved by adding excess quantities of Me_2SO_4 (5.0 eq. relative to 2VP repeat units) to the superstructures in DI water. To superstructures with short (3.8 μg, 3.6×10^{-5} mmol 2VP monomer unit), medium (7.6 μg, 7.2×10^{-5} mmol 2VP monomer unit), and long (15 μg, 1.4×10^{-4} mmol 2VP monomer unit) PFS_{25}-*b*-$P2VP_{500}$ segments was added Me_2SO_4 [(23 μg, 1.8×10^{-4} mmol), (46 μg, 3.6×10^{-4} mmol), and (92 μg, 7.2×10^{-4} mmol) respectively] and the resulting samples were aged for 24 h. Based on the studies described below (see Figure S27 and associated text), it is likely that quaternization involves a mixture of methylation and protonation.

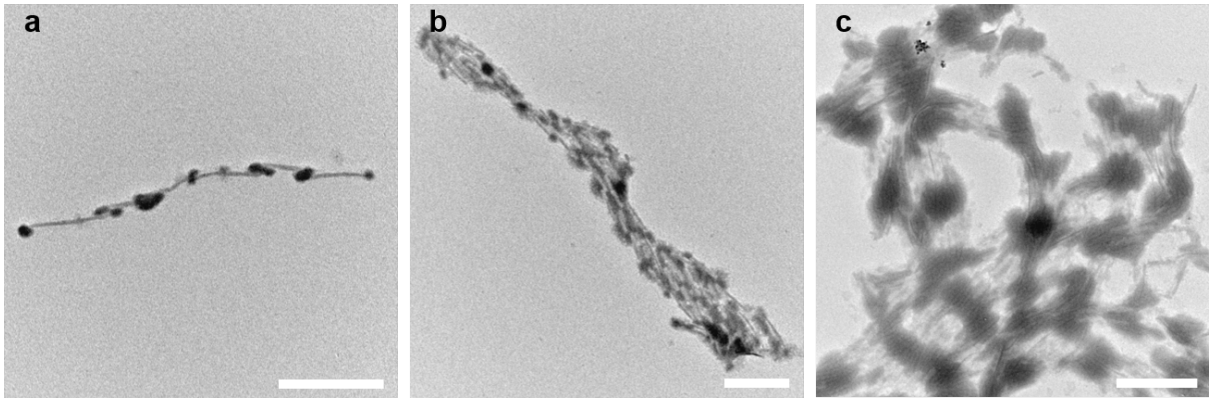


Figure S26. TEM micrographs showing the formation of cylindrical micelle-based superstructures upon the dialysis of B-A-B amphiphilic triblock comicelles with (a) short (L_n = 371 nm, L_w = 381 nm, L_w/L_n = 1.02, σ/L_n = 0.16), (b) medium (L_n = 459 nm, L_w = 469 nm, L_w/L_n = 1.02, σ/L_n = 0.14), and (c) long (L_n = 675 nm, L_w = 684 nm, L_w/L_n = 1.01, σ/L_n = 0.12) PFS_{25}-*b*-$P2VP_{500}$ segments against DI water. Scale bars 500 nm.

Quantification of degree of quaternization of P2VP using Me_2SO_4

Our initial attempt involved quaternization of B-A-B amphiphilic block comicelles in water, following the aforementioned procedure, and performing ^{1}H NMR on the purified and freeze-dried cylinders that were suspended in D_2O. However, due to the weak signal intensity, arising from low cylinder concentration, no meaningful data was obtained. For this reason, a P2VP homopolymer (M_n = 18000 g/mol, PDI = 1.50) was used as a model to quantify the degree of quaternization under identical conditions to those used to quaternize cylindrical block comicelles in both i-PrOH and DI water.

In two vials, P2VP homopolymer (20 mg, 1.1×10^{-3} mmol) was either dissolved in i-PrOH (5 mL) or suspended in DI water (5 mL). Subsequently, Me_2SO_4 (95 μL, 1.0 mmol, 5.0 equiv. relative to 2VP repeat unit) was added and the samples were stirred at room temperature for 18 h. During this time, formation of white solid in i-PrOH and dissolution of polymer in DI water was observed. The samples were separately transferred to two dialysis membranes (12000-14000 MWCO) and dialyzed against DI water for 24 h with multiple dialysate changes to remove excess Me_2SO_4. Water was then removed by freeze-drying and the remaining solids were analyzed by ^{1}H NMR (Figure S27b).

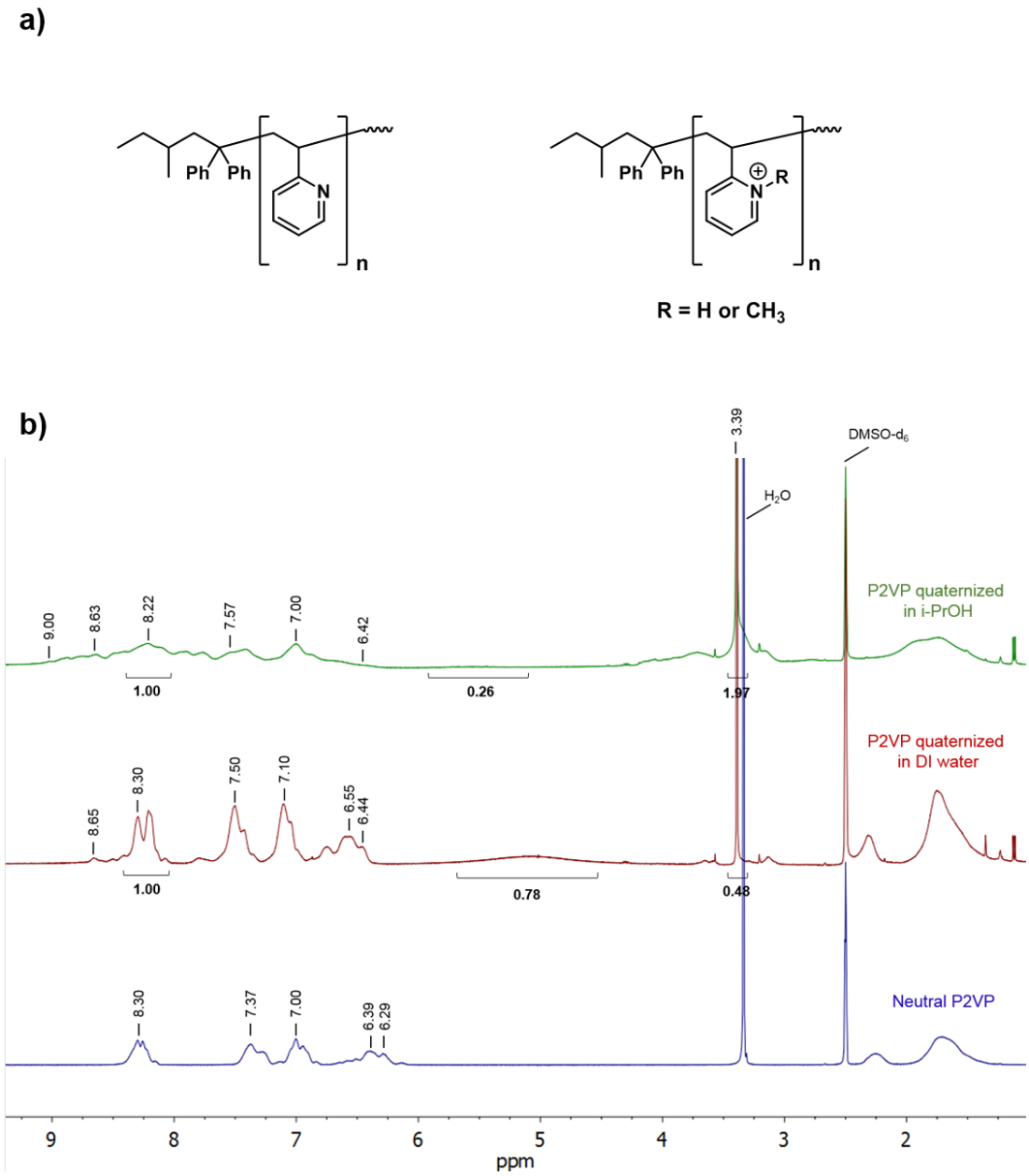


Figure S27. a) Chemical structures of neutral P2VP (left) and quaternized P2VP (right); b) ^{1}H NMR spectra of neutral P2VP (M_n = 18000 g/mol, PDI = 1.50) (blue spectrum), P2VP quaternized in DI water (brown spectrum), and P2VP quaternized in i-PrOH (green spectrum) acquired in DMSO-d_6.

As can be seen in Figure S27b, neutral P2VP shows four sets of main peaks in the aromatic region corresponding to the pyridine rings (blue spectrum). After quaternization, both samples show the emergence of a new peak at 3.39 ppm which corresponds to the methyl groups on the pyridine rings after the reaction. In addition, disappearance of the peaks at 6.29 and 6.39 ppm in the neutral P2VP after the reaction with Me_2SO_4 indicates a high degree of quaternization. Close examination of the P2VP sample quaternized in DI water (brown

spectrum) shows the existence of a new broad peak ~ 4.40 – 5.80 ppm which can be attributed to protonation of the pyridine rings. This suggests the initial hydrolysis of Me_2SO_4 in water and subsequent protonation of the pyridine rings. Integration analysis of this spectrum (relative integration of the peaks at ~ 4.40 – 5.80 and 3.39 ppm) revealed ca. 16% methylation and 78% protonation of the P2VP upon reaction with Me_2SO_4. On the other hand, similar integration analysis of the sample quaternized in i-PrOH suggests ca. 66% methylation and 26% protonation of P2VP homopolymer upon reaction with Me_2SO_4. This also accounts for the existence of more peaks in the aromatic region for the P2VP sample quaternized in i-PrOH compared to the one quaternized in DI water. It should be noted that the degree of polymerization of P2VP in polar solvents (such as DMF) using Me_2SO_4 has been reported to be more than 80%.[8]

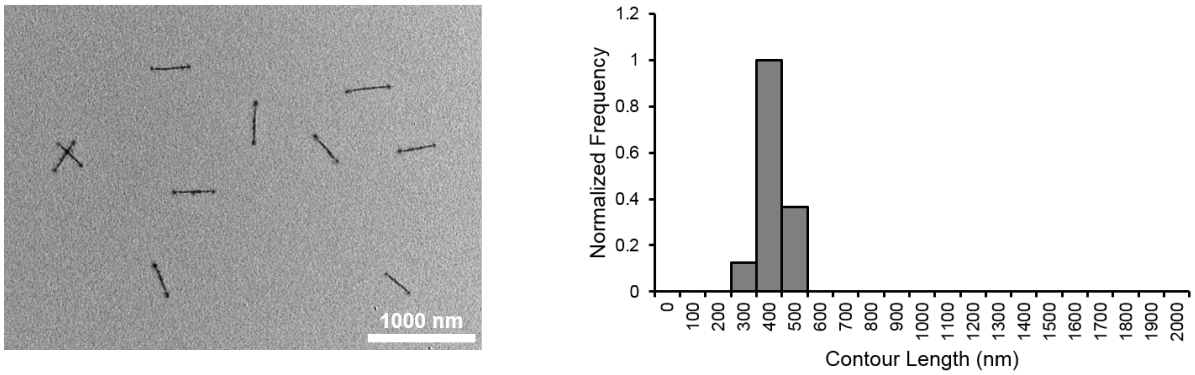


Figure S28. TEM micrograph of water-soluble triblock comicelles (L_n = 367 nm, L_w = 374 nm, L_w/L_n = 1.02, σ/L_n = 0.14) formed by the addition of 10 μg of PFS_{25}-*b*-$P2VP_{500}$ to 20 μg of PFS-*b*-(PEO-*g*-TEG) cylinders in i-PrOH (L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) followed by their dialysis against water and quaternization using Me_2SO_4 (left) and length histogram of the resulting cylindrical micelles (right).

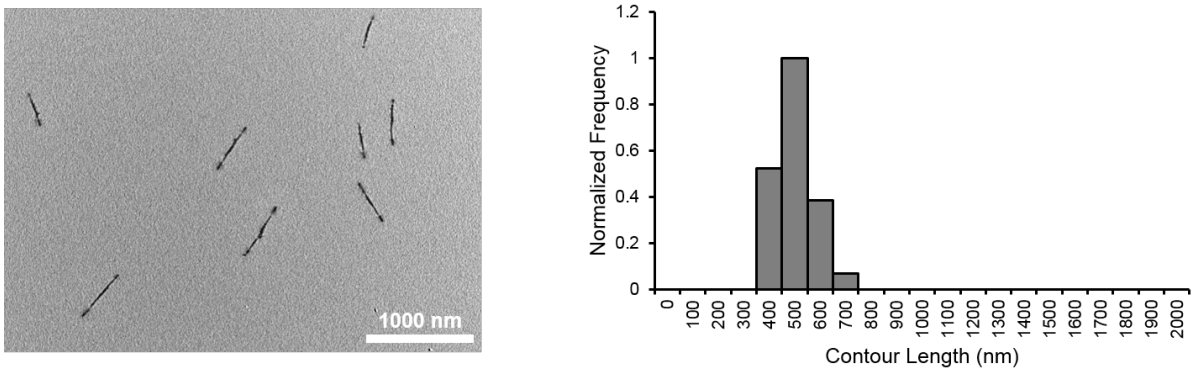


Figure S29. TEM micrograph of water-soluble triblock comicelles (L_n = 451 nm, L_w = 462 nm, L_w/L_n = 1.02, σ/L_n = 0.16) formed by the addition of 20 μg of PFS_{25}-*b*-$P2VP_{500}$ to 20 μg of PFS-*b*-(PEO-*g*-TEG) cylinders in i-PrOH (L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) followed by their dialysis against water and quaternization using Me_2SO_4 (left) and length histogram of the resulting cylindrical micelles (right).

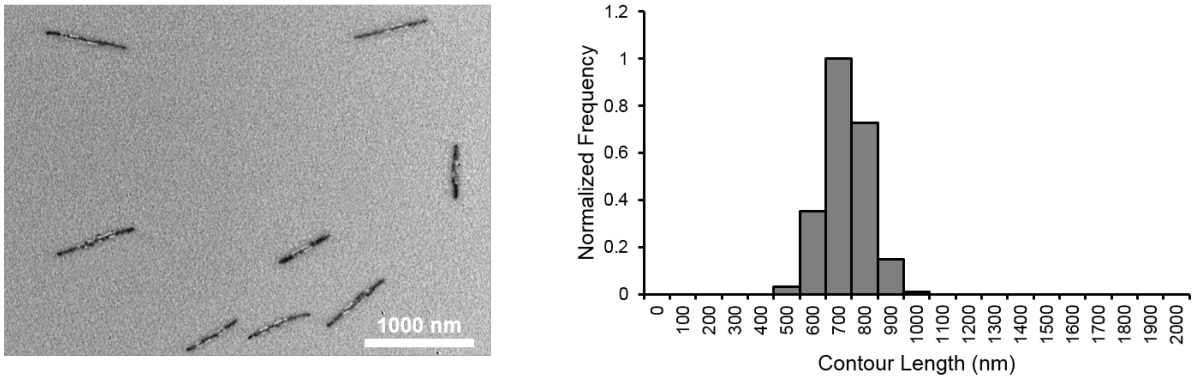


Figure S30. TEM micrograph of water-soluble triblock comicelles (L_n = 678 nm, L_w = 688 nm, L_w/L_n = 1.02, σ/L_n = 0.12) formed by the addition of 40 μg of PFS_{25}-*b*-$P2VP_{500}$ to 20 μg of PFS-*b*-(PEO-*g*-TEG) cylinders in i-PrOH (L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) followed by their dialysis against water and quaternization using Me_2SO_4 (left) and length histogram of the resulting cylindrical micelles (right).

DNA immobilization by quaternized triblock comicelles

The biorelevance of the water-soluble triblock comicelles was initially studied by their quaternization in i-PrOH followed by the addition of DNA and their final dialysis against water. To 0.2 mL of the above-mentioned triblock comicelles with short PFS_{25}-*b*-$P2VP_{500}$ segments (L_n = 371 nm, L_w = 381 nm, L_w/L_n = 1.02, σ/L_n = 0.16) in i-PrOH (3.8 μg, 3.6×10^{-5} mmol 2VP monomer unit) was added Me_2SO_4 (23 μg, 1.8×10^{-4} mmol, 5.0 eq. relative to 2VP

monomer units) and the resulting sample was aged for 24 h. The resulting sample was dialyzed against i-PrOH for 24 h to remove excess Me_2SO_4. To this sample was then added the commercially available native double-stranded DNA (purified from salmon testes, in its sodium salt form) containing ca. 2000 base pairs, purchased from Sigma-Aldrich, (38 μg, 10 eq. w/w) as a solution in DI water (6 mg/mL, 6.3 μL) and the resulting mixture was aged for 24 h. An aliquot of this solution of drop-cast and used for TEM analysis. The sample was then transferred to a 3500 g/mol MWCO dialysis membrane and dialyzed against DI water (200 mL) for 24 h with two changes of the dialysate to replace i-PrOH with water.

In a subsequent experiment, to study the DNA complexation by quaternized triblock comicelles with smaller quantities of DNA (1.0 and 0.5 eq. w/w relative to 2VP monomer units), the above-mentioned quaternized cylinders in i-PrOH were first dialyzed against DI water. To two vials containing dispersions of these cylinders in DI water (3.8 μg, 3.6×10^{-5} mmol 2VP monomer unit) were added 1.0 equivalent (3.8 μg, 3.8 μL) and 0.5 equivalent (1.9 μg, 1.9 μL) of DNA solution in DI water (1 mg/mL). The resulting samples were aged overnight and subsequently analyzed by TEM and zata potential analyses.

Zeta potential measurements of the quaternized triblock comicelles and DNA-coated triblock comicelles in DI water were performed using a Zetasizer Nano ZS instrument from Malvern Instruments using a disposable folded capillary zeta cell. We note that zeta potential results reported herein correspond to the entire system and not only the DNA-cylinder hybrids. As a result, these values are more representative of these hybrids when limiting quantities of DNA in Figure 5, Figure S34, and Figure S35 are used. Attempts to further characterize the cylinder-DNA hybrids using gel electrophoresis experiments were unsuccessful. However, in all cases, including the blank, reference DNA, severe smearing of the samples prevented us from more precisely characterizing these materials. This is a result of the nature of the DNA used in these proof-of-concept experiments.

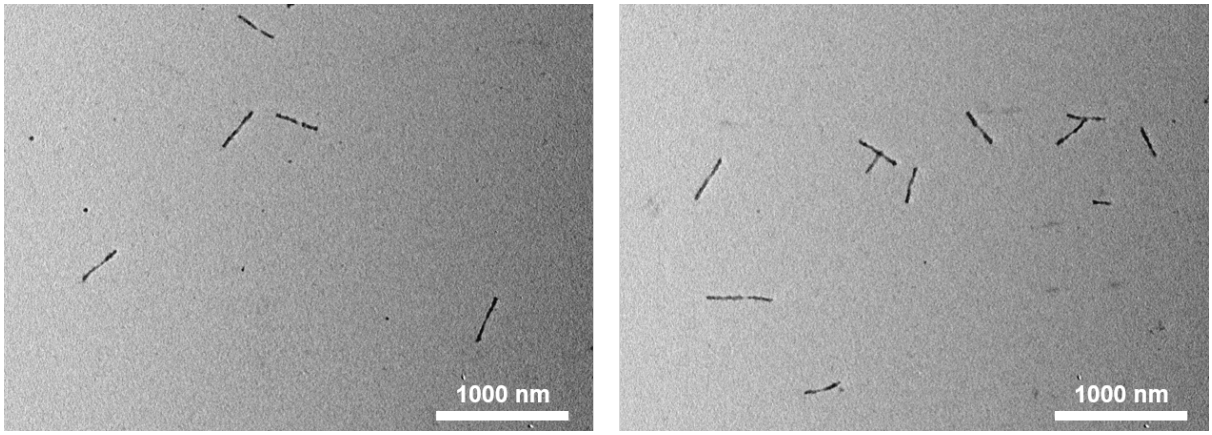


Figure S31. Additional TEM micrographs of DNA-coated triblock comicelles in i-PrOH.

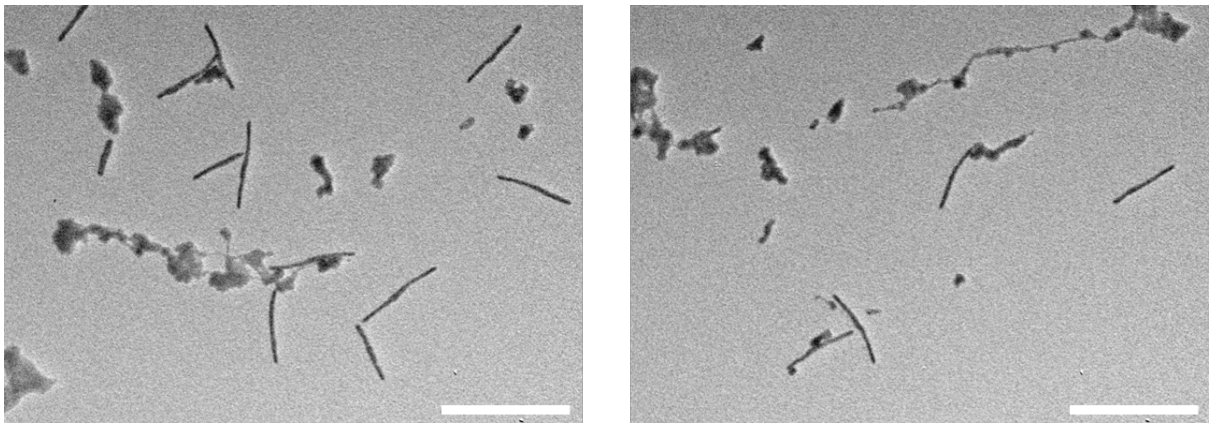


Figure S32. TEM micrographs showing the control experiment in which PFS-*b*-(PEO-*g*-TEG) homomicelles (20 μg, L_n = 240 nm, L_w = 253 nm, L_w/L_n = 1.06, σ/L_n = 0.24) were mixed with DNA (10-fold w/w) in i-PrOH. This shows that DNA strands do not tend to attach to the surface of neutral cylindrical micelles. Scale bars 500 nm.

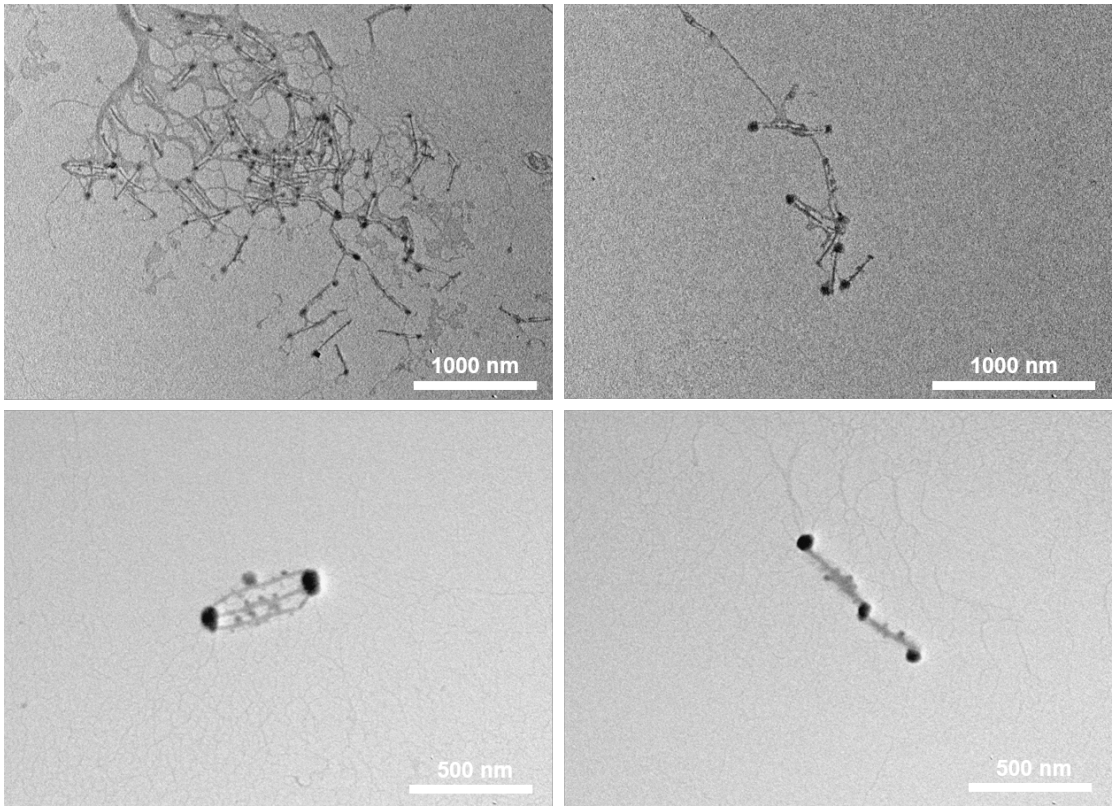


Figure S33. Additional TEM micrographs of DNA-coated triblock comicelles which were initially formed in i-PrOH and subsequently dialyzed against DI water showing the formation of both DNA-cylinder network structure and cylinder dimer/trimers.

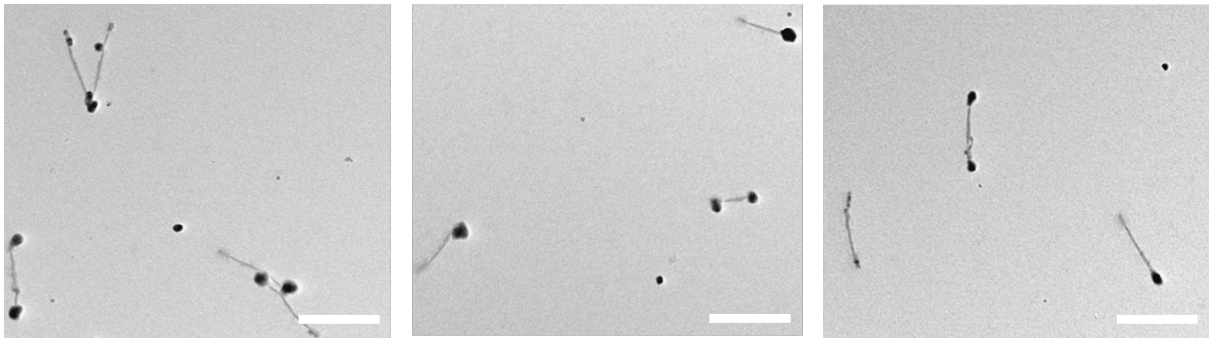


Figure S34. TEM micrographs showing partial coating of the positively charged segments of quaternized triblock comicelles in DI water with DNA strands by adding 0.5 equivalent (w/w relative to PFS_{25}-*b*-$P2VP_{500}$) of DNA to water-soluble triblock comicelles (L_n = 367 nm, L_w = 374 nm, L_w/L_n = 1.02). Scale bars 500 nm.

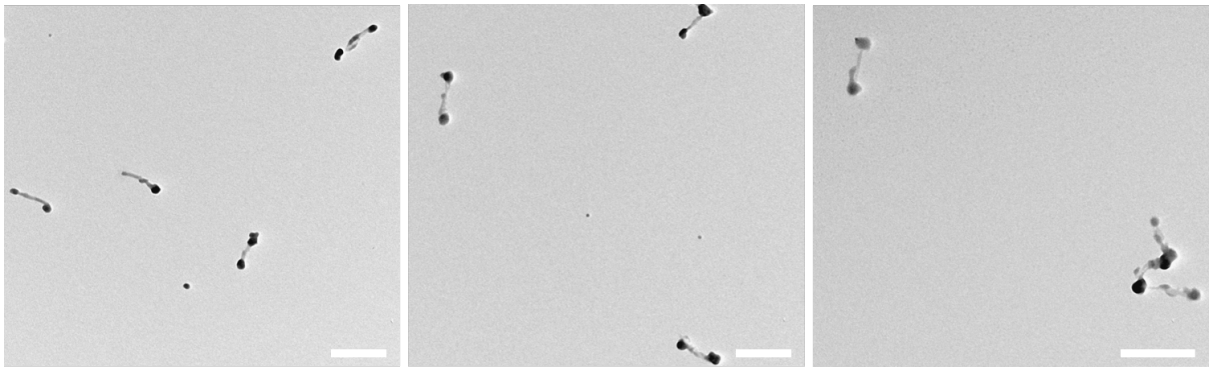


Figure S35. TEM micrographs showing near-complete coating of the positively charged segments of quaternized triblock comicelles in DI water with DNA strands by adding 1 equivalent (w/w relative to PFS_{25}-*b*-$P2VP_{500}$) of DNA to water-soluble triblock comicelles (L_n = 367 nm, L_w = 374 nm, L_w/L_n = 1.02). Scale bars 500 nm.

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